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(19) (CA) **CANADIAN PATENT** (12)

(54) AIDS FOR THE CONDITIONING STEP IN THE HOT WATER  
EXTRACTION PROCESS FOR TAR SANDS

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"IMPROVED AIDS FOR THE CONDITIONING STEP IN  
THE HOT WATER EXTRACTION PROCESS FOR TAR SAND"

ABSTRACT OF THE DISCLOSURE

5           Aqueous solutions of inorganic alkaline substances,  
such as NaOH, are contacted with bitumen or analogous organic matter  
to produce solutions, emulsions, or mixtures containing surfactants  
beneficial in the conditioning step in the hot water process for the  
extraction of bitumen from bituminous sands. Such solutions, emulsions,  
or mixtures may be added to the conditioning step of the hot water  
10       extraction process in place of some or all of the conditioning aids  
employed according to the prior art, for the more economical operation  
of the process.

BACKGROUND OF THE INVENTION

The invention relates to the hot water extraction process for extracting bitumen from tar sand. More particularly alternative processing aids are set forth herein that may be used in the tar sand conditioning step of said hot water process to replace  
5 some or all of the inorganic alkaline substance heretofore employed as a processing aid.

As readily-available supplies of conventional crude oil get used up, the oil industry has turned to tar sand deposits as  
10 a source of hydrocarbons. The main tar sand deposit on the North American continent is in the Fort McMurray region of the Province of Alberta in Canada, in an area traversed by the Athabasca River, and this deposit is being actively developed at the commercial level to contribute to Canada's hydrocarbon supplies.

15 Tar sand is essentially a mixture of sand grains, water, salts, fine mineral solids of the particle size of clay minerals, and a heavy oil usually referred to as bitumen. It is the bitumen that is of commercial interest. Tar sand also goes by the names of oil sand and bituminous sand. Although the composition varies throughout the  
20 deposit, speaking generally, the main constituents analyse at,

oil	11.59% by weight
water	4.41% by weight
solids	84.00% by weight

In theory, there are advantages in extracting the  
25 bitumen in situ since such processes obviate the need for mining and associated materials handling of huge tonnages of tar sand and tailings, the equipment for which requires large amounts of capital. In practice, however, mining of tar sand followed by isolating the bitumen therefrom by the hot water extraction process is the preferred commercial method  
30 because in spite of the problems of mining and materials handling, bitumen recovery is very high, normally around 93%.



According to the hot water extraction process as commonly practiced, mined tar sand is added to a conditioning drum horizontally mounted and capable of rotation about its longitudinal axis. Such conditioning drum is hereinafter referred to as the tumbler. As well  
5 as the tar sand, hot water (referred to as slurry water), steam and, for most tar sand feeds, relatively minor amounts of NaOH are also added to the tumbler. Steam is normally added as two streams, first in relatively large amounts at the front end of the tumbler, and subsequently in the form of trim steam via sparging valves set in small-bore pipes passing  
10 along the length of the inside of the tumbler, to provide more delicate temperature adjustment. The NaOH commonly added assists in the conditioning action, and is used for all tar sand types except the very rich material, that is, for all tar sands of bitumen content less than about 12% bitumen. Commonly, for every 3250 tons of tar sand one adds  
15 610.30 tons of water and such steam as to give a final conditioning temperature in the range of 150° to 180°F, although the process may be operated outside this temperature range.

It is usual for the rate of feed to be set such that it takes less than 10 mins. for tar sand to pass through the tumbler from  
20 the inlet to the outlet end. During this time the bitumen is dislodged from the sand particles so that what enters as tar sand, with bitumen and sand tightly bound together (with interstitial water connate to the deposit probably also involved in such bonding), leaves as a mixture, with bitumen, sand, and water merely in loose association, and in such  
25 a state that, should suitable conditions be provided, the sand and the bitumen will separate severally from the mixture. This operation in the tumbler is commonly called 'conditioning'. On emerging from the tumbler, the tumbler is screened to remove oversized debris such as rocks and lumps of undigested tar sand, and diluted with further hot water (called  
30 flood water). The diluted slurry then is subjected to the first tar sand components separation step, termed primary separation. This operation is

conducted in a primary separation vessel.

The primary separation vessel is a vessel wherein screened diluted slurry is maintained in a quiescent condition. The screened, diluted slurry is discharged into the central region of the contained body  
5 of slurry with the following effects:

Most of the sand, especially the coarse sand, sinks to the bottom and may be pumped out as an aqueous tailings stream; The bitumen in the form of globules, becomes aerated by attachment of air bubbles present in the primary separation  
10 vessel and being rendered buoyant thereby rises to the surface of the vessel where it is collected as a froth (primary froth);

Bitumen that fails to get aerated, along with much of the fine mineral matter, collectively having a density close  
15 to that of the aqueous contents of the vessel, has little tendency to either sink or rise and so remains in the central region of the vessel.

The mixture of unaerated bitumen, water and fine solids (collectively known as "middlings") contains valuable amounts of bitumen  
20 that it is advantageous to recover. Hence a portion of the middlings is continuously withdrawn to obtain a further yield of bitumen therefrom. The middlings portion thus withdrawn is advanced to subaerated flotation cells where it is vigorously agitated with air to produce a second froth (secondary froth) and a further tailings stream (secondary tailings).

It is advantageous to operate the circuit in such a way as  
25 to cause as much of the bitumen as possible to report to the primary froth because the purity of said primary froth is high. Typically, primary froth contains 66.40% by weight of bitumen while secondary froth has only 23.78% bitumen and also contains such large quantities of entrained water  
30 and fine minerals that it should be cleaned in a froth settler. After the cleaning step, the secondary froth is combined with the primary froth and the bitumen is recovered out of the combined froth.

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5 The conditioning of the tar sand that occurs in the tumbler has a marked influence in determining the tendency of the bitumen to join the primary froth. Traditionally, process aids such as sodium hydroxide and sodium silicate, that is, alkaline compounds of monovalent metals, have been added to the tumbler to improve recovery. The present invention is directed toward providing other compounds effective as process aids that are compatible with the traditionally-used substances and may be employed in place of part or all of such traditional conditioning aids, and which result in considerable savings in costs. Since a commercial tar sand processing plant, for producing 125,000 barrels of synthetic crude oil per day, uses about 35,566 tons per year of sodium hydroxide solution at a specific gravity of 1.22 at an annual cost of between \$4 million and \$5 million (1977 Canadian dollars), a significant reduction of NaOH consumption is desirable.

#### SUMMARY OF THE INVENTION

15 I have discovered that the addition of sodium hydroxide solution in its raw state to the tumbler is an inefficient use of this chemical for most tar sand types. By contrast, sodium hydroxide that has been contacted with bitumen or an analogous organic material, on being added to the tumbler, has enhanced power to contribute to the recovery of bitumen from tar sand, said enhanced power being reflected in similar levels of bitumen recovery from tar sand at reduced caustic usage. In consequence, considerably less sodium hydroxide need be used after such contact.

25 For example, raw sodium hydroxide is commonly used at the rate of about 0.03% by weight expressed as a proportion of tar sand feed. When bitumen is vigorously mixed or emulsified with sodium hydroxide solution however, a rate of sodium hydroxide addition of 0.01% gives approximately the same level of bitumen recovery. Since most of the bitumen added as the organic phase of the emulsion is subsequently recovered along with the bitumen from the tar sand, this bitumen is merely recycled in the process and no significant loss in that respect occurs.

30 It is my theory that the mechanism by which sodium hydroxide

aids conditioning in the tumbler is one whereby surfactants are produced by interaction of the sodium hydroxide with organic substances. These surfactants produced in situ in the tumbler assist in dislodging the bitumen out of the tar sand, allowing the bitumen ultimately to report to the primary froth of the primary separation vessel. If such speculation is correct, it may further be said that the tumbler residence time of less than 10 minutes, which is the commonly practiced period for conditioning tar sand, is too short a time for the theoretical minimum quantity of sodium hydroxide to produce a desired level of surfactants in the tumbler; thus excess sodium hydroxide must be used. When however, according to the invention, sodium hydroxide is held in contact with bitumen or analogous organic material for a relatively prolonged period of time or intimately mixed there with, higher concentrations of surfactants appear to be formed. If thereafter this sodium hydroxide/organic material mixture is used as a process aid in the tar sand tumbler, it is considerably more effective than sodium hydroxide alone.

The preferred embodiment of this invention involves using bitumen emulsified with aqueous sodium hydroxide solution as a process aid. The emulsion may be used, when necessary, in conjunction with extra sodium hydroxide solution. The emulsion may be prepared by mixing bitumen, sodium hydroxide, and hot water in a simple mixing tank, in-line mixer or similar device.

Another possible embodiment involves contacting sodium hydroxide solution, preferably with vigorous mixing, with tar sand. The resulting solution or emulsion may then be used as a process aid.

Another possible embodiment involves using refinery spent caustic to form the processing aid. Said spent caustic contains dissolved phenols and analogous organic acidic compounds in the form of sodium salts. Their presence in the tumbler allows a large portion or all of the raw sodium hydroxide of the prior art to be dispensed with.

What all these embodiments have in common is intimate contact between sodium hydroxide and bitumen or other organic matter for a sufficient period of time to permit the sodium hydroxide to react with components of the organic matter to produce a desirable level of surfactants, said surfactants being beneficial to the conditioning of tar sand in the hot water process. Other alkali metal substances, for instance potassium hydroxide, may be used in place of sodium hydroxide, but there would be no economic advantage in doing so. Other organic matter than bitumen may be used to provide components for the organic moiety in the surfactants, the limitation being that the surfactants should not add obnoxious substances to the process tailings, that might adversely affect the environment, or to the synthetic crude oil that is the eventual product of the bitumen isolated from the tar sand.

Broadly stated the invention is an improvement in the hot water process for extracting bitumen from tar sand wherein tar sand is mixed with hot water to form a slurry and retained in a rotating tumbler for a period of time to condition said slurry. The improvement comprises adding as a process aid a surfactant prepared outside the tumbler by mixing an alkali metal hydroxide with organic material.

20

#### DESCRIPTION OF THE PREFERRED EMBODIMENT

The invention is exemplified by the following extraction experiments, in which a series of additives were added to water and tar sand in a vessel and stirred, to approximate the process in a tumbler, and then held quiescent to approximate the process in a primary separation



vessel. More particularly, the experiments were performed in a batch extraction apparatus. To a 1.5 L stainless steel vessel were added hot water (0.14 L) to act as slurry water and then tar sand (500 g), followed by such additives as are listed in the Table below. The vessel was  
5 provided with a heated jacket, to maintain the contents at the desired temperature (180°F), and with a variable speed agitator. The slurry was agitated at 600 r.p.m. for 10 minutes, 1 L of hot water was added (flood water), and the mixture was stirred for an additional 10 minutes. Then the  
10 agitator was stopped and the resulting bituminous froth was skimmed from the surface. (The single vessel laboratory procedure and the froth produced by it have been shown to be reasonably analogous to the tumbler-primary separation vessel procedure, as practiced in a pilot plant, and to the froth produced by said pilot plant.)

#### Preparation of Emulsions

15 To 145 g water held at 80 to 90°C in a stainless steel vessel fitted with an impeller-type agitator was added 1 ml of 1 N NaOH solution and then the quantity of bitumen or bitumen froth called for in the example. The mixture was stirred vigorously to react the components. This mixture was used as slurry water in the runs to extract bitumen  
20 from tar sand.

#### Preparation of Tailings Concentrate

Secondary tailings collected from the process to extract bitumen from tar sand were evaporated in a laboratory-scale rotary evaporation apparatus under mild vacuum until reduced to one tenth their  
25 original volume. The resultant concentrate was used as slurry water in extraction tests.

TABLE I

	Comments	Process Aid	Amount of Process Aid (using 500 g tar sand)	Bitumen Recovery via Primary Froth (wt% of total bitumen in tar sand feed)
5				
	Typical example using NaOH under normal conditions	sodium hydroxide	0	34
10			3 ml of 1 N (0.024 wt% NaOH on tar sand)	76
			5 ml of 1 N (0.04 wt% NaOH on tar sand)	89
15				
	Shows how the amount of NaOH required to achieve a given recovery is reduced by prior mixing of NaOH with bitumen and bitumen froth	sodium hydroxide	1 ml of 1 N (0.008 wt% NaOH on tar sand)	79
20			3 ml of 1 N (0.024 wt% NaOH on tar sand)	88
25		bitumen/NaOH	1 ml of 1 N NaOH mixed with 5 g bitumen	84
		bitumen froth/NaOH	1 ml of 1 N NaOH mixed with 5 g bitumen froth from average tar sand (1 wt% bitumen expressed on tar sand feed)	83
30				
35		bitumen froth/NaOH	1 ml of 1 N NaOH mixed with 5 g bitumen froth from rich tar sand	86
		bitumen froth/NaOH	1 ml of 1 N NaOH mixed with 5 g bitumen froth from high fines tar sand	91
40				
	Shows increased recoveries when NaOH is replaced by concentrating tailings water	No additive	0	60
45		unconcentrated secondary tailings	145 ml (added as slurry water and flood water)	59
50		concentrated secondary tailings (reduced to 1/10 initial volume)	145 ml (added as slurry water)	87

TABLE I (continued)

	Comments	Process Aid	Amount of Process Aid (using 500 g tar sand)	Bitumen Recovery via Primary Froth (wt% of total bitumen in tar sand feed)
5				
			0	34
		Refinery spent caustic	1 ml neat	55
10	Shows how NaOH can be replaced by refinery spent caustic (largely organic sulfonates)		3 ml neat	83
			5 ml neat	90

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR  
PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. In the hot water process for extracting bitumen from tar  
sand wherein tar sand is mixed with hot water to form a slurry and  
5 retained in a rotating tumbler for a period of time to condition said  
slurry, the improvement which comprises:  
adding as a process aid a surfactant prepared outside the  
tumbler by mixing an alkali metal hydroxide with organic material.
2. The improvement as set forth in claim 1 wherein:  
10 the organic material is bitumen and it is mixed with an  
aqueous solution of sodium hydroxide.
3. The improvement as set forth in claim 1 wherein:  
the organic material is bitumen contained in tar sand and the  
latter is mixed with an aqueous solution of sodium hydroxide.
- 15 4. The improvement as set forth in claim 1 wherein:  
the organic material is bitumen contained in slurry previously  
produced by the hot water process and said slurry is mixed with an aqueous  
solution of sodium hydroxide.
5. The improvement as set forth in claim 1 wherein:  
20 said process aid is refinery spent caustic containing  
surfactant.
6. The improvement as set forth in claim 1 wherein:  
said process aid is secondary tailings from the hot water  
process, concentrated before use.
- 25 7. The improvement as set forth in claim 1 wherein:  
the process aid is bituminous froth obtained from the hot  
water process.

